Reactivity of Tetramethylphosphonium Fluoride in Acetonitrile Solutions

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Anhydrous tetramethylphosphonium fluoride dissolved in acetonitrile reacts slowly with the solvent under formation of (*E*)-2-amino-1-cyano-propene which was characterized by infrared and NMR spectroscopy. An attempted preparation of $[Me_3PF_3]^-$ by addition of Me_3PF_2 to Me_4PF/acetonitrile solutions has shown that the desired reaction does not occur, but prolonged reaction times and small acetonitrile concentrations lead to the formation of the iminophosphorane $Me_3P{=}NC(Me){=}CH_2$ and $[Me_4P]^+HF_2{}^-$. $Me_3P{=}NC(Me){=}CH_2$ was characterized by infrared spectroscopy and a single-crystal structure determination. *N*-(2-propenyl)trimethyliminophosphorane crystallizes in the monoclinic space group $P2_1/c$ with $a = 1006.8(2)$, $b = 1523.5(3)$, $c = 1180.3(2)$ pm, $\beta = 111.72(6)^\circ$ and $Z = 8$. The two independent molecules per unit cell have nearly planar P=N-C(C)=C skeletons with torsion angles P–N–C–C of 5.9(3)° and 7.1(4)° and an average P=N distance of 158.1(2) pm. The general ability of Me_4PF as a fluoride donor was proven by the reaction with SO_2 which results in the formation of $[Me_4P]^+SO_2F^-$. The colorless salt was characterized by infrared, Raman, and NMR spectroscopy.

Key words: Iminophosphorane, Vibrational Spectroscopy, NMR Spectroscopy, Crystal Structure

Introduction

Since the report of an anhydrous Me_4NF by Christe *et al.* in 1990, the syntheses of several salts with novel anions have demonstrated the exceptional reactivity of the fluoride anion in this so-called “naked” fluoride [1 – 10]. The unusual reactivity was explained with the cesium effect as a consequence of the unfavorable combination of a large cation and a small anion [11, 12]. Therefore several anhydrous fluorides with larger organic cations than $[Me_4N]^+$ have been described with the aim of obtaining a more “naked” fluoride [13 – 18]. However, it has not been demonstrated that these compounds serve as better sources for the “naked” fluoride than Me_4NF.

Another explanation for the reactivity of the “naked” fluoride ion sources is their solubility in aprotic solvents like acetonitrile. According to this explanation, the role of the large organic cations is rather an increase of the solubility of the fluoride salts. The nakedness of the fluoride ion in solutions should then depend rather upon the solvent than the counterion [19]. Most of the salts with novel anions have been prepared with Me_4NF in the presence of acetonitrile as solvent [2 – 10]. Christe *et al.* have shown that solutions of Me_4NF in acetonitrile are only stable for a short period. At r. t. acetonitrile is attacked by the fluoride anion within a few hours. The reaction goes along with the formation of Me_4NHF_2 and (*E*)-2-amino-1-cyano-propene and a change in color from colorless to brown [20].

In the course of our studies on methylfluorophosphoranes we have reported on the structural properties of Me_4PF [18]. It has an ionic structure in the solid state with weak interactions between cations and anions and therefore it should be a promising source for “naked” fluoride. Moreover, the compound possesses unique properties compared to other sources of “naked” fluoride. The salt is volatile in vacuum, and the gas phase and solutions in nonpolar solvents possess a phosphorane structure of Me_4PF with an exceptionally weak P–F_{ax} bond. Besides the structural properties, the chemistry of Me_4PF is unexplored [18, 21, 22]. Me_4PF could serve as a better source of “naked” fluoride than Me_4NF, but the nakedness of the fluoride could also be decreased by the bonding isomerism which is impossible for Me_4NF. We report herein our studies of Me_4PF as fluoride donor in acetonitrile solutions.

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Table 1. Infrared frequencies (cm^{-1}) of $NH_2C(Me)=CHCN \cdot Me_4PF$, $NH_2C(Me)=CHCN \cdot Me_4NF$ and the $[Me_4X]^+$ cations (X = N, P).

$H_2NC(Me)=CHCN$ $\cdot Me_4PF$	$[Me_4P]^+$ [24]	$H_2NC(Me)=CHCN$ $\cdot Me_4NF$ [1]	$[Me_4N]^+$ [24]	Assignment $[Me_4X]^+$	Assignment $NH_2C(Me)=CH\text{-}CN$
3195 m		3200 br			$\nu(NH_2)$
		3030 m	3011 m	$\nu_{as}(CH_3)$	$\nu_{as}(CH_3)$
2971 m	2964 m	2975 m		$\nu_{as}(CH_3)$	$\nu_{as}(CH_3)$
	2873 vw		2954 vw	$\nu_s(CH_3)$	
2179 m		2180 s			$\nu(C\equiv N)$
1579 m		1588 m			$\nu(C=C)$
1440 ms	1414 w	1497 m	1483 s	$\delta_{as}(CH_3)$	
		1428 m	1402 m	$\delta_s(CH_3)$	
		1374 vw			
1299 s	1288 m	1311 w	1293 w	}$\delta_s(CH_3)$, $\rho(CH_3)$	
1286 ms, br		1254 w			
1169 ms		1186 m			
1087 w		1083 w			ν (C-N)
1006 vvs	991 vs	1028 w		}$\rho(CH_3)$	
976 sh					
		962 s	945 vs	}$\nu_{as}(C_4N)$	
		949 s			
898 m		915 mw			ν (C-C)
		847 vw			
791 s	774 m			}$\nu_{as}(C_4P)$	
778 s					
703 m		717 s			
		600 w			
532 ms		538 m			
501 ms		505 m			
		469 m	456 m	$\delta_{as}(C_4N)$	
407 m		412 w			
363 m		369 w			
336 m					
288 m	276 m			$\delta_{as}(C_4P)$	

Results and Discussion

Reaction of Me_4PF with acetonitrile

Me_4PF is remarkably soluble (0.7 mol L^{-1}) in acetonitrile. Freshly prepared acetonitrile solutions of Me_4PF display in the ^{19}F NMR spectrum only one signal at -70 ppm, which is typical for the fluoride ion [20]. After standing for 6–8 h at r. t. a very weak doublet at -149 ppm ($^1J_{HF}$ = 131 Hz) for the HF_2^- anion appears. The intensity of the HF_2^- peak in the ^{19}F NMR spectrum increases during further standing at r. t. and after 2 d reaches a level of *ca.* 5 % of the fluoride peak intensity. The increase of the HF_2^- peak is accompanied by a change of the color of the solution from colorless to yellow. In the ^{31}P NMR spectra only the typical multiplet for the $[Me_4P]^+$ cation at 24.8 ppm ($^2J_{PH}$ = 15 Hz) is observed, but the ^{13}C NMR spectra display additional signals at 19.4, 54.6, 125.1 and 166.1 ppm, the intensities of which increase simultaneously. The ^{13}C NMR resonances are comparable to those of (E)-2-amino-1-cyano-propene [23].

The formation of HF_2^- indicates a reaction between Me_4PF and acetonitrile as it was observed for Me_4NF in acetonitrile solutions [1, 19]. Hydrogen abstraction occurs resulting in the formation of CH_2CN^- followed by its reaction with acetonitrile in accordance with Eqs. 1 and 2.

$$CH_3CN + 2F^- \rightarrow CH_2CN^- + HF_2^- \quad (1)$$

$$\begin{aligned} &CH_2CN^- + CH_3CN + HF_2^- \\ &\rightarrow H_2N(CH_3)C{=}C(H)CN + 2F^- \end{aligned} \quad (2)$$

From the yellow solution a microcrystalline solid starts to precipitate after two days. When after standing for 2 weeks at r. t. the solvent is removed in dynamic vacuum, the remaining yellow microcrystalline solid consists, according to its infrared spectra, of Me_4PF and (E)-2-amino-1-cyano-propene together with traces of $[Me_4P]^+HF_2^-$. Since Me_4PF cannot be removed from the resulting mixture, despite its sufficient vapor pressure, we assume that it forms an adduct with (E)-2-amino-1-cyano-propene similarly as it has been reported for $Me_4NF \cdot H_2N(CH_3)C{=}C(H)CN$. The

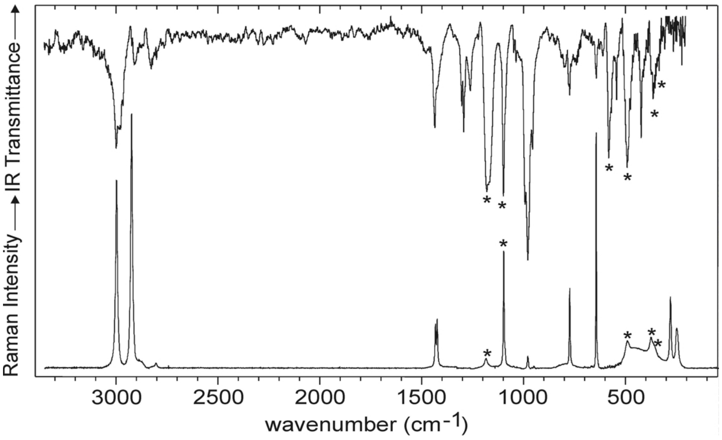

Fig. 1. Infrared and Raman spectrum of $[Me_4P]^+SO_2F^-$. Vibrations of the SO_2F^- anion are marked with an asterisk.

formation of an 1 : 1 adduct is indicated by the yield of the resulting solid. The infrared frequencies of $Me_4PF \cdot H_2N(CH_3)C{=}C(H)CN$ are compared with those of $Me_4NF \cdot H_2N(CH_3)C{=}C(H)CN$ in Table 1. In both adducts the vibrations of the tetrahedral $[Me_4P]^+$ and $[Me_4N]^+$ cations, respectively, appear at their typical frequencies [24]. The infrared bands of the $H_2N(CH_3)C{=}C(H)CN$ molecule in the Me_4PF adduct agree with those observed for the Me_4NF adduct. A detailed assignment of the vibrations of the $H_2N(CH_3)C{=}C(H)CN$ molecule is difficult due to its size and low symmetry. Therefore only the stretching modes which appear in their typical regions have been assigned. Especially the intense $\nu(C{\equiv}N)$ at 2180 cm^{-1} is characteristic for the $H_2N(CH_3)C{=}C(H)CN$ molecule and therefore very useful for checking its presence in the adduct with Me_4PF.

Reaction of Me_4PF with SO_2

Sulfur dioxide has been chosen as a weak Lewis acid in order to probe whether Me_4PF is generally able to serve as a fluoride ion donor. The low fluoride ion affinity of SO_2 (-43.8 kcal mol^{-1}) marks a limit of Lewis acidity which is sufficient for fluoridation reactions with common fluorides such as alkali metal fluorides. Me_4PF reacts with gaseous SO_2 at r. t. vigorously under formation of a yellow solid which is partially soluble in liquid SO_2. A moderate reaction is observed during the melting of Me_4PF in a ten-fold molar amount of SO_2 or when acetonitrile is used as the solvent. In both cases the fluorosulfite salt is formed quantitatively (Eq. 3).

$$[Me_4P]^+F^- + SO_2 \rightarrow [Me_4P]^+SO_2F^- \qquad (3)$$

The colorless microcrystalline $[Me_4P]^+SO_2F^-$ rapidly decomposes on contact with moisture according to Eq. 4.

$$\begin{aligned} &4[Me_4P]^+SO_2F^- + H_2O \\ &\rightarrow 2[Me_4P]^+HF_2^- + [Me_4P^+]_2S_2O_5^{2-} + 2SO_2 \end{aligned} \qquad (4)$$

Thermal decomposition occurs at 75 °C and leads to a yellow solid of a similar composition as it was formed by the reaction of Me_4PF with gaseous SO_2 at r. t. The decomposition is different and more complex than for $[Me_4N]^+SO_2F^-$ where, as a first step, a simple dissociation into SO_2 and the fluoride has been observed. In the case of $[Me_4P]^+SO_2F^-$, besides an insoluble yellow solid, $[Me_4P]^+HF_2^-$ and $[Me_4P]^+SO_3F^-$ have been identified as decomposition products.

$[Me_4P]^+SO_2F^-$ is soluble in acetonitrile and liquid SO_2. The solutions display in the ^{19}F NMR spectrum a singlet at 102 ppm which is typical for the SO_2F^- anion [10]. The infrared and Raman spectra are shown in Fig. 1. The assignments for the $[Me_4P]^+$ cation were made according to well-known literature data [24]. An unambiguous identification of the SO_2F^- anion is possible, since the vibrations of the highly symmetric cation appear in typical regions and can easily be separated from those of the anion. The vibrations of the SO_2F^- anion are listed in Table 2 and assigned according to our previous studies on fluorosulfites [12]. It should be noted that the preparation of $[Me_4P]^+SO_2F^-$ in acetonitrile solution has not led to the formation of $H_2N(CH_3)C{=}C(H)CN$ as a by-product.

Reaction of Me_4PF with Me_3PF_2/acetonitrile

The Lewis acid-base properties of methylfluorophosphoranes Me_nPF_{5-n} ($n = 1-4$) display a dra-

Table 2. Vibrational frequencies (cm^{-1}) of the fluorosulfite anion.

$[\mathrm{Me_4P}]^+\mathrm{SO_2F}^-$		$[\mathrm{Me_4N}]^+\mathrm{SO_2F}^-$ [12]		$\mathrm{K}^+\mathrm{SO_2F}^-$ [12]		
IR	Raman	IR	Raman	IR	Raman	Assignment
1184 s	1189 (4)	1187 s	1196 (4)	1179 s	1187 (20)	$\nu_5(A'')\nu_{\mathrm{as}}(\mathrm{SO_2})$
1104 s	1102 (23)	1103 s	1105 (23)	1099 m	1109 (100)	$\nu_1(A')\nu_{\mathrm{s}}(\mathrm{SO_2})$
586 s		590 m	592 (5)	596 s	597 (9)	$\nu_2(A')\nu(\mathrm{SF})$
498 s	496 (4)	498 s	494 (2)	504 s	500 (18)	$\nu_3(A')\delta(\mathrm{OSO})$
372 w	381 (6)	383 w	383 (7)	381 m	388 (42)	$\nu_4(A')\delta_{\mathrm{s}}(\mathrm{OSF})$
358 sh	360 sh	359 w	363 (16)	366 m	370 (31)	$\nu_6(A'')\delta_{\mathrm{as}}(\mathrm{OSF})$

matic change within the series. Our previous studies have shown that $\mathrm{MePF_4}$ has typical properties of a Lewis acid [25]. The Lewis acidity of $\mathrm{Me_2PF_3}$ is lower than that of $\mathrm{MePF_4}$ and comparable to that of $\mathrm{MePF_3H}$ [26, 27]. Overall, this is an expected trend in which $\mathrm{PF_5}$ has the highest Lewis acidity, and substitution of a fluorine atom by a methyl group or a hydrogen atom leads to a decrease in Lewis acidity. The Lewis acid-base properties of $\mathrm{Me_3PF_2}$ are not known yet, but $\mathrm{Me_4PF}$ is already a strong fluoride donor as shown by the reaction with $\mathrm{SO_2}$. This implies a low Lewis acidity of $\mathrm{Me_3PF_2}$ which might only react with more powerful fluoridating agents and therefore serve as a useful probe for reactivity studies on sources for "naked" fluoride.

Attempted preparations of $\mathrm{Cs}^+[\mathrm{Me_3PF_3}]^-$ by the reaction of well-ground activated CsF with $\mathrm{Me_3PF_2}$ have only resulted in the isolation of the unchanged starting materials, regardless of whether acetonitrile was used as solvent or not. Similar results were obtained when $\mathrm{Me_4PF}$ or $\mathrm{Me_4NF}$ were mixed with neat $\mathrm{Me_3PF_2}$. When acetonitrile solutions of $\mathrm{Me_4PF}$ or $\mathrm{Me_4NF}$ were mixed with an equivalent amount of $\mathrm{Me_3PF_2}$ no hint was found for the formation of $\mathrm{Me_3PF_3}^-$ salts. Prolonged standing of such solutions at r. t. led only to the known reaction of the fluoride with acetonitrile under formation of $\mathrm{Me_4NF}\cdot\mathrm{H_2N(CH_3)C{=}C(H)CN}$ and $\mathrm{Me_4PF}\cdot\mathrm{H_2N(CH_3)C{=}C(H)CN}$, respectively.

In the case of $\mathrm{Me_4PF}$ we observed an unexpected reaction when a large excess of $\mathrm{Me_3PF_2}$, which also served as a solvent, and a small amount of acetonitrile ($\mathrm{Me_4PF}:\mathrm{CH_3CN} = 1:5$) were used. Prolonged standing of such solutions at r. t. led to the formation of colorless cubic crystals which have been identified by structure analysis as *N*-(2-propenyl)trimethyliminophosphorane and characterized by infrared spectroscopy. The infrared spectrum shows the absence of $[\mathrm{Me_4P}]^+$ salts and of $\mathrm{H_2N(CH_3)C{=}C(H)CN}$. For the assignment of the vibrational frequencies, the infrared spectra of $\mathrm{Me_3PNH}$ and $\mathrm{Me_3PNCH_3}$ have been considered [28, 29]. The infrared spectrum of *N*-(2-propenyl)trimethyliminophosphorane displays the vibrations of the methyl groups in their typical regions. The $\nu(\mathrm{C{=}C})$ at 1590 cm^{-1} of the propenyl group coincides with that of $\mathrm{H_2N(CH_3)C{=}C(H)CN}$, but the presence of the latter can be excluded due to the absence of its typical and intense C≡N stretching mode. Most characteristic for the iminophosphorane are the intense infrared band of $\nu(\mathrm{P{=}N})$ at 1230 cm^{-1} (in $\mathrm{Me_3PNMe}$ at 1239 cm^{-1}) [29] and the P-C stretching modes at 682 and 634 cm^{-1} which appear in their typical regions (620 – 730 cm^{-1}).

The precipitation of *N*-(2-propenyl)trimethyliminophosphorane is accompanied by the formation of $[\mathrm{Me_4P}]^+\mathrm{HF_2}^-$ which remains in the $\mathrm{Me_3PF_2}$/acetonitrile solution. Furthermore, the solution contains only small amounts of unreacted $\mathrm{Me_4PF}$ and traces of $\mathrm{H_2N(CH_3)C{=}C(H)CN}$. The identified products suggest a reaction according to Eq. 5a. However, a Wittig olefination of acetonitrile according to Egs. 5b, c is the most likely mechanism.

$$2[\mathrm{Me_4P}]^+\mathrm{F}^- + \mathrm{CH_3CN} \rightarrow \mathrm{Me_3P{=}N\text{-}C(CH_3){=}CH_2} + [\mathrm{Me_4P}]^+\mathrm{HF_2}^- \tag{5a}$$

$$2[\mathrm{Me_4P}]^+\mathrm{F}^- \rightarrow \mathrm{Me_3P{=}CH_2} + [\mathrm{Me_4P}]^+\mathrm{HF_2}^- \tag{5b}$$

$$\mathrm{Me_3P{=}CH_2} + \mathrm{CH_3CN} \rightarrow \mathrm{Me_3P{=}N\text{-}C(Me){=}CH_2} \tag{5c}$$

Crystal structure of $\mathrm{Me_3P{=}NC(Me){=}CH_2}$

The crystal data are summarized in Table 3. *N*-(2-Propenyl)trimethyliminophosphorane crystallizes in the monoclinic space group $P2_1/c$ with 8 formula units per unit cell. Selected bond lengths and angles of $\mathrm{Me_3P{=}NC(Me){=}CH_2}$ are summarized in Table 4. The asymmetric unit shown in Fig. 2 consists of two symmetry-independent molecules which show only small differences in bond lengths and angles. The P=N and C=C bond lengths are found in their typical regions [30]. In the two independent

Table 3. Crystallographic data of $Me_3PNC(Me)CH_2$.

Formula	$C_6H_{14}NP$
M_r, $g mol^{-1}$	131.40
Crystal size, mm^3	$0.08 \times 0.06 \times 0.05$
Crystal system	monoclinic
Space group	$P2_1/c$ (no. 14)
a, pm	1006.8(2)
b, pm	1523.5(3)
c, pm	1180.3(2)
β, deg	111.72(6)
V, 10^6 pm^3	1681.9(6)
Z	8
D_{calcd}, $g cm^{-3}$	1.04
Temperature, °C	20
μ (MoK_α), cm^{-1}	2.4
$F(000)$, e	576
θ range, deg	2.56 – 24.99
hkl range	±11, ±18, ±14
Refl. measured / unique / R_{int}	5487 / 2891 / 0.0528
Refl. with $I \geq 2\sigma(I)$	1223
Param. refined	257
$R1/wR2^a$ $[I \geq 2\sigma(I)]$	0.0376 / 0.0683
$R1/wR2^a$ (all data)	0.1160 / 0.0781
GoF[b] on F^2	0.719
$\Delta\rho_{fin}$ (max / min), e 10^6 pm^{-3}	0.11 / −0.17

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o{}^2, 0) + 2F_c{}^2)/3$ and A and B are constants adjusted by the program; [b] GoF $= S = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{obs} - n_{param})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

molecules the P=N and C=C double bonds are arranged *cis* with torsion angles of 5.9 and 7.1°, respectively. Overall, the molecules are slightly distorted away from C_s symmetry with an almost coplanar arrangement of the propenyl carbon atoms, the P=N group and one *P*-bonded methyl carbon atom.

Conclusion

Anhydrous tetramethylphosphonium fluoride dissolved in acetonitrile reacts slowly with the solvent with formation of (*E*)-2-amino-1-cyano-propene. The presence of $[Me_4P]^+HF_2{}^-$ in the reaction mixture indicates that acetonitrile reacts with fluoride under hydrogen abstraction resulting in the formation of CH_2CN^- which reacts further with another acetonitrile molecule. A different reaction occurs when a large excess of Me_3PF_2, which also serves as a solvent, and a small amount of acetonitrile ($Me_4PF : CH_3CN = 1:5$) are used. Prolonged standing of such solutions at r. t. lead to the formation of *N*-(2-propenyl)trimethyliminophosphorane and $[Me_4P]^+HF_2{}^-$.

Table 4. Selected bond lengths (pm) and angles (deg) of $Me_3PNC(Me)CH_2$.

P(1)–N(1)	158.3(2)	C(11)–P(1)–C(13)	106.7(3)
P(1)–C(11)	179.1(4)	C(12)–P(1)–C(13)	105.1(2)
P(1)–C(12)	177.4(4)	N(2)–P(2)–C(21)	115.2(2)
P(1)–C(13)	178.4(4)	N(2)–P(2)–C(22)	116.6(2)
N(1)–C(14)	138.3(3)	N(2)–P(2)–C(23)	107.1(2)
C(14)–C(15)	149.4(5)	C(21)–P(2)–C(22)	104.6(3)
C(14)–C(16)	131.8(3)	C(21)–P(2)–C(23)	107.8(3)
P(2)–N(2)	157.8(2)	C(22)–P(2)–C(23)	104.8(2)
P(2)–C(21)	179.3(4)	C(14)–(N1)–P(1)	124.8(2)
P(2)–C(22)	177.2(4)	C(24)–(N2)–P(2)	125.8(2)
P(2)–C(23)	180.7(3)	N(1)–C(14)–C(15)	112.1(4)
N(2)–C(24)	136.8(3)	N(1)–C(14)–C(16)	127.8(3)
C(24)–C(25)	150.0(3)	C(15)–C(14)–C(16)	120.1(4)
C(24)–C(26)	132.7(3)	N(2)–C(24)–C(25)	112.9(3)
N(1)–P(1)–C(11)	114.8(2)	N(2)–C(24)–C(26)	129.1(3)
N(1)–P(1)–C(12)	106.7(2)	C(25)–C(24)–C(26)	118.0(4)
N(1)–P(1)–C(13)	116.3(2)	P(1)–N(1)–C(14)–C(16)	5.9(3)
C(11)–P(1)–C(12)	106.4(3)	P(2)–N(2)–C(24)–C(26)	7.1(4)

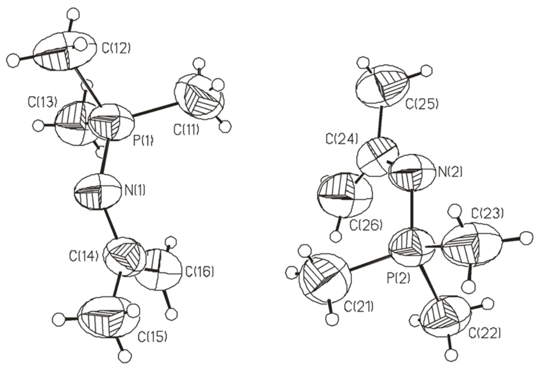

Fig. 2. Asymmetric unit of the unit cell of $Me_3PNC(Me)CH_2$ containing two crystallographically independent molecules. Displacement ellipsoids are drawn at the 50 % probability level.

Despite the formation of (*E*)-2-amino-1-cyano-propene, freshly prepared Me_4PF acetonitrile solutions can generally be used as fluoridating reagents. This has been demonstrated by the reaction with sulfur dioxide which results in the formation of $[Me_4P]^+SO_2F^-$. Attempted preparations of $[Me_3PF_3]^-$ salts by the reaction of Me_3PF_2 with CsF, Me_4PF or Me_4NF have shown that the Lewis acidity of Me_3PF_2 is too low to form the $Me_3PF_3{}^-$ anion. This result completes our previous studies on the Lewis acid-base properties of methylfluorophosphoranes Me_nPF_{5-n} (n = 1 – 4), which display a dramatic change within the series. Starting with PF_5 as a strong Lewis acid, the substitution of a fluorine atom by a methyl group leads to a decrease in Lewis acidity, such that Me_3PF_2 already has no Lewis acidic properties, while Me_4PF finally displays only Lewis base properties.

Experimental Section

Apparatus and materials

All synthetic work and sample handling were performed employing standard Schlenk techniques and a standard vacuum line (stainless steel or glass). Organic solvents were dried by standard methods. The synthesis of Me_4PF was carried out by literature methods [18]. Trimethyldifluorophosphorane was prepared by the reaction of Me_3PS with SbF_3 [31].

Infrared spectra were recorded on a Bruker IFS 113v spectrophotometer. Spectra of dry powders were obtained using a CsBr plate coated with the neat sample. The Raman spectra were recorded on an ISA T64000 spectrometer using an Ar^+ laser tube (514.5 nm) from Spectra Physics and a glass cell. The NMR spectra were recorded with a Bruker DBX 300 spectrometer with 85 % H_3PO_4, $CFCl_3$ and TMS as standards.

Reaction of Me_4PF with acetonitrile

Into a 25 mL glass vessel with a grease-free valve charged with 0.20 g (1.8 mmol) Me_4PF 5 g acetonitrile was condensed at −196 °C. After warming to r. t. a colorless solution was obtained (0.3 mL of the solution was transferred into an NMR tube for parallel NMR investigations). The solution became yellow after one day, and after standing for 2 weeks at r. t. the volatiles were removed in dynamic vacuum. The remaining yellow microcrystalline solid (340 mg, 98 % yield) consisted, according to NMR and infrared spectra, of $H_2NC(Me){=}CHCN \cdot Me_4PF$ and traces of $[Me_4P]^+HF_2^-$. – ^{13}C NMR ($[D_6]$acetone) for (*E*)-2-amino-1-cyano-propene: δ = 19.1 (s, $-C(CH_3)_2-$), 54.6 (s, C=C-CN), 125.1 ppm (s, CN), 166.1 ppm (s, $C{=}C(NH_2)-$).

Synthesis of $[Me_4P]^+SO_2F^-$

Me_4PF (0.21 g; 1.91 mmol) was placed into a 25 mL glass vessel with a grease-free valve. After condensation of 1 g (15.6 mmol) SO_2 at −196 °C, the mixture was warmed slowly to r. t. After 1 h excess SO_2 was removed in dynamic vacuum. The weight of the colorless residual (0.33 g) represented a quantitative yield of $[Me_4P]^+SO_2F^-$. – IR (neat): $\nu_{as}(CH_3)$ 3012 s, $\nu_s(CH_3)$ 2913 w, $2\delta_{as}(CH_3)$ 2843 w, $\delta_{as}(CH_3)$ 1445 m, $\delta_s(CH_3)$ 1313 m, $\delta_s(CH_3)$ 1273 w, $\nu_{as}(SO_2)$ 1184 s, $\nu_s(SO_2)$ 1104 s, $\rho(CH_3)$ 983 vs, $\rho(CH_3)$ 954 s, $\rho(CH_3)$ 806 w, $\nu_{as}(C_4P)$ 778 w, $\nu_s(C_4P)$ 652 w, $\nu(SF)$ 586 s, 549 m, $\delta(SO_2)$ 498 s, 428 m, $\delta_s(OSF)$ 372 w, $\delta_{as}(OSF)$ 358 sh. – Raman: $\nu_{as}(CH_3)$ 2998 s, $\nu_s(CH_3)$ 2924 s, 2804 vw, $\delta_{as}(CH_3)$ 1438 m, $\delta_{as}(CH_3)$ 1428 m, $\nu_{as}(SO_2)$ 1189 w, $\nu_s(SO_2)$ 1102 s, $\rho(CH_3)$ 985 w, $\nu_{as}(C_4P)$ 779 s, $\nu_s(C_4P)$ 650 s, $\delta(SO_2)$ 496 m, $\delta_s(OSF)$ 381 m, $\delta_{as}(OSF)$ 360 sh, $\delta_{as}(C_4P)$ 286 m, $\delta_s(C_4P)$ 256 m.

Synthesis of N-(2-propenyl)trimethyliminophosphorane

Into a 25 mL glass vessel with a grease-free valve charged with 0.10 g (0.9 mmol) Me_4PF 0.20 g (5 mmol) acetonitrile and 2.4 g (21 mmol) trimethyldifluorophosphorane were condensed at −196 °C. After warming to r. t. a colorless solution was obtained. While the solution was kept at r. t. for 20 d, colorless crystals grew on the walls of the vessel. After the separation of the solution, 0.05 g (59 % yield) of *N*-(2-propenyl)trimethyliminophosphorane was obtained. The volatiles were removed from the separated solution in dynamic vacuum. The remaining colorless solid (0.01 g) consisted, according to infrared spectra, of $[Me_4P]^+HF_2^-$ and traces of $H_2NC(Me){=}CHCN \cdot Me_4PF$. – IR (neat): $\nu(CH_3)$ 3047 m, $\nu(CH_3)$ 2970 w, $\nu(CH_3)$ 2905 w, 1675 w, $\nu(C{=}C)$ 1590 m, $\delta(CH_3)$ 1433 m, $\delta(CH_3)$ 1398 m, $\delta(CH_3)$ 1290 m, $\nu(P{=}N)$ 1230 s, $\rho(CH_3)$ 1185 mw, $\rho(CH_3)$ 1095 m, 1071 w, 945 br, $\rho(CH_3)$ 880 m, $\nu(C_3P)$ 682 m, $\nu(C_3P)$ 634 w, 546 ms, 288 m, 256 m.

Crystal structure determination

Single crystals were placed in Lindemann capillaries in a cooled stream of dry nitrogen, and the X-ray diffraction studies were carried out using an Enraf Nonius Kappa CCD diffractometer. For the data reduction, structure solution and refinement, SCALE PACK, programs in the SHELXTL package and PARST were used [32–35]. The phosphorus atoms were located by Patterson Methods. All atoms including protons were found in difference Fourier syntheses, and the final refinement was carried out with anisotropic (except for H atoms) displacement parameters. Table 3 summarizes the crystal data and details pertinent to data collection and structure refinement.

CCDC 761560 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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